

Mixed-Matrix Membranes for CO₂ and H₂ Separations Using Metal-Organic Frameworks and Mesoporous Hybrid Silicates

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OBJECTIVES

The objectives of this project are to explore the use of metal-organic frameworks and mesoporous hybrid silicas in polymer-based mixed-matrix membranes for CO₂ and/or H₂ gas separations. A goal is to exploit the high surface areas, adsorption capacities and selectivities of these nanoporous additives to achieve unprecedented transport of gases critical to energy conservation and emerging clean energy technology.

ACCOMPLISHMENTS TO DATE

1) Polymer-based mixed-matrix membranes incorporating metal-organic frameworks.

Nanometer-sized particles of Cu(II) biphenyl dicarboxylate triethylenediamine or Cu(II) BPDC-TED (Figure 1) were synthesized using a procedure developed by Yaghi et al. Procedures published by Yaghi et al. and Huang et al. were followed to prepare micrometer-sized and nanometer-sized crystals of MOF-5, respectively (Figure 2). Cu(II) BPDC-TED is known to preferentially adsorb methane whereas MOF-5 has reported selectivity for hydrogen.

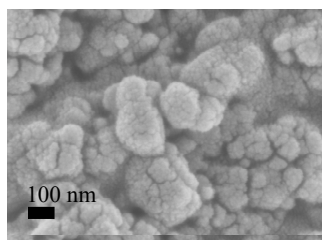


Figure 1. SEM image of Cu(II) BPDC-TED metal-organic framework.

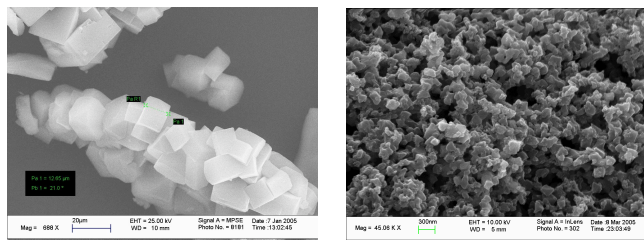


Figure 2. SEM images of MOF-5 prepared using two procedures, Yaghi's (left) and Huang's (right).

Cu(II) BPDC-TED was incorporated into various rubbery polymers including polydimethylsiloxane (PDMS), poly(3-octylthiophene) (POT), and poly(3-(2-acetoxyethylthiophene) (PAET). At a 30% (w/w) loading in both PDMS and POT, the MOF acted as a filler causing a decrease in permeability for each gas tested (N₂, O₂, CH₄, CO₂) that was accompanied by a negligible change in selectivity. At the same 30% (w/w) loading, PAET, the polymer with the lowest inherent permeability, experienced a two-fold increase in CH₄ permeability owing to the increased solubility of methane in the ~12 Å MOF pore (Table 1). At least for this MOF, low permeability polymers are required to observe facilitated transport of methane by the mixed-matrix membranes.

Table 1. Permeability^a and Selectivity Values for Cu(II) BPDC-TED/PAET Mixed-Matrix Membranes at 35 °C

Membrane	%MOF	N ₂	O ₂	CH ₄	CO ₂	H ₂	O ₂ /N ₂	CO ₂ /CH ₄	CH ₄ /N ₂
PAET	0	0.05	0.24	0.08	1.41	N/A	4.8	17.6	1.6
Cu/PAET	30	0.07	0.26	0.16	1.34	3.33	3.7	8.4	2.3

^a Permeability coefficient: 1 Barrer = 10⁻¹⁰[cm³ (STP)-cm/cm²-sec-cm Hg].

2) Polymer-based mixed-matrix membranes incorporating mesoporous hybrid silicas.

Periodic mesoporous organosilica in polymer membranes. Mesoporous benzene-silica (MBS), an ordered

benzene-silica hybrid material, has a hexagonal array of mesopores with a lattice constant of 52.5 Å, and crystal-like pore walls that exhibit structural periodicity with a spacing of 7.6 Å along the channel direction. The pore wall of MBS is hydrophobic which we anticipated would be analogous to the MOF but with larger pores that would allow better penetration by Matrimid polymer chains. Pure gas permeation tests (Table 2) showed the biggest increase for hydrogen followed by CO₂. Other periodic mesoporous organosilicas with bridging ethane and ethylene groups were dispersed in Matrimid with similar results.

Table 2. Permeability^a and Selectivity Values for MBS/Matrimid Membranes at 35

	%MBS	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄
pure Matrimid	0	17.50	0.22	1.46	0.21	7.29	79.55	6.64	34.71
MBS/Matrimid	10	32.94	0.32	2.55	0.24	13.83	104.11	8.06	58.59
MBS/Matrimid	20	36.33	0.52	2.96	0.40	16.35	70.41	5.74	40.99
MBS/Matrimid	30	40.12	0.63	3.57	0.46	19.99	63.52	5.65	43.36

^a Permeability coefficient: 1 Barrer = 10⁻¹⁰[cm³ (STP)-cm/cm²-sec-cm Hg].

Microporous mesoporous materials (MMM) in polymer membranes. MMM can be prepared by using preformed zeolite seeds as framework building units which results in a material that has both mesopores and micropores. If MMM is used in polymer membranes, the mesopores can provide good contact with the polymer while the micropores can provide size selectivity. Preliminary pure gas permeation tests (Table 3) showed improvement in hydrogen transport and selectivity. Lower loadings suggest that methane transport is also possible. Mesoporous Silicalite-1 (0.55nm), LTA (0.4nm) and Y (0.73nm) were also prepared and are under evaluation.

Table 3. Permeability^a and Selectivity Values for ZSM-5/MCM-48/Matrimid Membranes at 35

	%ZSM-5/MCM-48	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄
pure Matrimid	0	17.50	0.22	1.46	0.21	7.29	79.55	6.64	34.71
ZSM-5/MCM-48	10	22.34	0.16	1.66	0.15	5.47	137.29	10.22	35.98
ZSM-5/MCM-48	20	23.43	0.16	1.57	0.18	3.62	145.86	9.76	20.19
ZSM-5/MCM-48	30	67.00	0.52	5.41	0.37	17.14	128.57	10.39	46.61

^a Permeability coefficient: 1 Barrer = 10⁻¹⁰[cm³ (STP)-cm/cm²-sec-cm Hg].

FUTURE WORK

Membranes prepared using MOF-5 will be characterized and tested for H₂ separations. Additional metal-organic frameworks and mesoporous hybrid silicas will be synthesized, characterized, and tested for CO₂ and H₂ separations.

LIST OF CONFERENCE PRESENTATIONS AND STUDENTS SUPPORTED UNDER THIS GRANT

“Methane Facilitated Transport Using Mixed-Matrix Membranes Containing Metal-Organic Frameworks”, Carlos Barcena, Hadi N. Yehia, Kenneth J. Balkus, Jr., John P. Ferraris, Inga H. Musselman, 60th Southwest Regional Meeting of the American Chemical Society, Fort Worth, TX, September 29-October 4, 2004.

“Methane Facilitated Transport Using Mixed-Matrix Membranes Containing Metal-Organic Frameworks”, Carlos Barcena, Hadi Yehia, Thomas J. Pisklak, Kenneth J. Balkus, Jr., John P. Ferraris, and Inga H. Musselman, Strategic Partnership for Research in Nanotechnology, Second Annual Conference, Richardson, TX, November 11-12, 2004.

“Gas Permeability Properties of Matrimid Membranes Containing the Mesoporous Benzene Silica”, Yanfeng Zhang, Inga H. Musselman, Kenneth J. Balkus, Jr., and John P. Ferraris, Strategic Partnership for Research in Nanotechnology, Second Annual Conference, Richardson, TX, November 11-12, 2004.

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